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Adsorption model equation for multi-component gas on coalbed and its assessment

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Abstract

The Langmuir isothermal model is most widely used model in Enhanced Coalbed Methane Recovery (ECBMR) simulation because of its simplicity and a certain level of its accuracy. But the model is literally applicable only to the isothermal condition. And the extended Langmuir model to binary or ternary gases does not necessarily correspond to experimental data.

The Dubinin-Astakhov (D-A) model and the Doong-Yang (D-Y) model applies to the non-isothermal condition, maintaining its simplicity. The former is the equation for a single component adsorbate gas and the latter is the equation for multi-component adsorbate gases. These models are containing parameters of the saturated vapor pressure in the equation. However, as methane and carbon dioxide in coalbed reservoir are in the supercritical state, the saturated vapor pressure of these gases is indefinable. In this study, the modification of the D-Y model which is sometimes made in the D-A model to enable it to apply to the supercritical state was made.

The comparison was made between the modified D-Y model and the experimental data which was obtained by displacement experiments for binary and ternary gases. Theoretical values calculated from the modified D-Y model gave close agreement with the experimental values and, especially in components less adsorbed. As a result, the modified D-Y model was promising model to predict amount of adsorbed and desorbed gas on coal matrix.

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Keywords: ECBMR, Langmuir model, Dubinin-Astakhov model, Doong-Yang model, Displacement experiment

1. Introduction

Enhanced Coalbed Methane Recovery (ECBMR) is the one of the key technology to address climate

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change as well as to increase fossil fuel recovery. Methane (CH_4) desorption caused by injected carbon dioxide (CO_2) adsorption on coal seam is the key phenomenon in ECBMR. CO_2 is injected into coal seam and adsorbed onto the surface of it and CH_4 is desorbed from coal surface and recovered simultaneously. In some cases, nitrogen (N_2) is also injected with CO_2 to relieve coal swelling which decreases coal permeability. As general idea, adsorption equation of CH_4, CO_2 and N_2 on coal and its parameters are decided by the experimental approach and used in the numerical simulator which has important role to estimate the amount of stored CO_2 and recovered CH_4 in ECBMR projects. Several adsorption equations for both a single gas and multi-component gases are proposed to predict experimental results.

2. Adsorption models

In the case of ECBMR simulator, the accuracy in the calculation of the adsorbed gas volume on coal seam and the simplicity which enables us to express it easily in the numerical simulator are required. The Langmuir adsorption isotherm [1] is only equation which is largely used in several numerical simulators because of its simplicity and relatively small error. The Langmuir adsorption isotherm is expressed as below,

$$Q = \frac{Q_{max} K P}{1 + K P} \quad (1)$$

where Q is the adsorbed gas volume, Q_{max} is the maximum adsorbed gas volume, K is the Langmuir coefficient and P is the pressure. In the case of multi-component gases, Eq. (1) is extended and equation for component i is below,

$$Q_i = \frac{Q_{max} K_i P_i}{1 + \sum_j K_j P_j} \quad (2)$$

Eq. (2) is called extended Langmuir model (EL model).

Accuracy of the Langmuir isotherm is not high comparing to other adsorption equations proposed, especially when more than two components flow in coal cleat system [2]. Additionally as the name implies, parameters in the Langmuir isotherm calculated from experimental data is available only for the specific temperature of the experiment conducted.

Dubinin-Astakhov model (D-A model) **Error! Reference source not found.** (Eq. (3)) is one of most commonly used model to express experimental results of adsorption and desorption on coal. D-A model is developed depending on the adsorption potential theory and its accuracy is much higher than other models proposed in research on ECBMR.

$$Q = Q_{max} \exp\left[-D \left(\ln \frac{P_s}{P}\right)^n\right] \quad (3)$$

where P_s is the saturated vapor pressure and D and n are the constant attained by adsorption experiments. The n takes the value between 1 and 3. D-A model is not available for adsorption of supercritical CO_2 and CH_4 which is naturally achieved in the subsurface condition because an equation of model contains the saturated vapor pressure which is indefinable in the supercritical condition. To treat this limitation of application of the model, the variables associated with the pressure in equation are modified to the variables of gas density [4] (Eq. (4)). It means convert form the set of the actual pressure and the saturated vapor pressure into the set of the adsorbed gas density and the gas density flowing around coal.

(4)

where and are the adsorbed phase density and the density of flowing gas, respectively.

To calculate the adsorbed amounts of binary or ternary gases using the D-A model, the extension of equation which is similar in Eq. (2) is necessary. Several studies addressed this issue and dealt with problem of treatment of maximum adsorption volume. Doong and Yang **Error! Reference source not found.** proposed the assumption that the adsorption volume of one adsorbate gas is decreased by the total adsorption volume of all other adsorbate gases. And parameters used in the equation are obtained by the result of single gas adsorption experiment. This assumption seems preferable to apply to the adsorption phenomenon on coal involving desorption.

(5)

where the subscript i and j mean gas components. Eq. (5) is named the Doong-yang model (D-Y model) in this study as a matter of convenience. Then it is extended to model for the supercritical condition, the modified D-Y model (mD-Y model),

(6)

Below is the mD-Y model for binary gases attained by solving Eq. (6) for components i and j.

(7)

where

(8)

The equation for ternary gases was also calculated.

(9)

3. Verification

Theoretical values calculated by the EL model and the mD-Y model were compared with experimental values obtained by displacement experiments using the volumetric method **Error! Reference source not found.**. The experimental setup is shown in Fig. 1. First, the single gas (CH_4, CO_2 or N_2) was injected into the evacuated sample cell. Next, the pressure change was measured and the adsorbed amount of the gas was calculated. The temperature was kept at 35 ˚C, the pressure was up to 6MPa. Results of absolute adsorption volume and the parameters needed in theoretical equations are shown in Fig. 2 and Table 1, respectively. The density at the standard boiling point was used as the adsorption phase density except for CO_2. For CO_2, the triple point was used because standard boiling point is indefinable. The Span and Wagner EOS [6] was chosen to calculate adsorption phase density. Experimental results were in excellent

agreement with both two models, especially modified D-A model indicated better fitting.

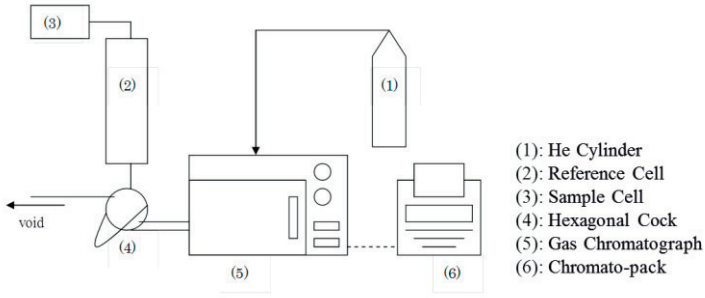

Fig. 1 Schematic diagram of the experimental apparatus

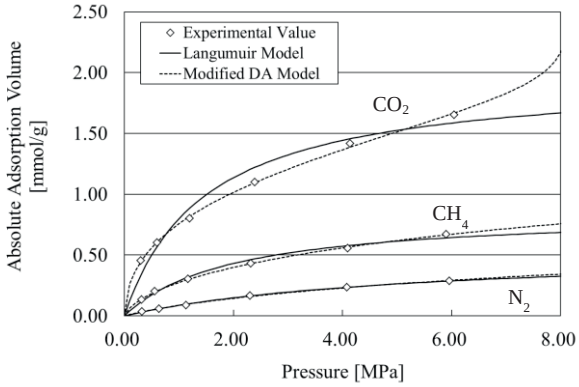

Fig. 2 Absolute adsorption volume from the single gas experiment

Table 1(a) Parameters of the Langmuir model and (b) Parameters of the D-A model

(a)

	K	Q_0	P_L
	[1/MPa]	[mmol/g]	[Pa]
CH_4	0.509	0.855	1.97E+06
CO_2	0.676	1.976	1.48E+06
N_2	0.191	0.538	5.24E+06

(b)

	D	V_0	n
	[-]	[mmol/g]	[-]
CH_4	0.1620	1.224	1.550
CO_2	0.1680	2.583	1.390
N_2	0.2210	0.742	1.560

Then theoretical values were compared with binary gases experiments. The experiment started from the condition that the sample cell was saturated with CH_4, and CO_2 was injected into sample cell. Theoretical values were calculated by the EL model (Eq. (2)), the mD-Y model when n is equal to two, which corresponds to Dubinin-Radushkevich equation for multi-component gases, and the mD-Y model when n is variable (Eq.(9)). The values of the absolute adsorption volume at the end of the experiment and theoretical values are shown in

Fig. 3. To compare the data quantitatively, the normalized root-mean-square-error (RMSE) defined below was introduced in this study.

(10)

where N is the number of experimental data and Q_e and Q_c are the adsorbed gas volume in the experiment and the calculation, respectively. Results of RMSEs are shown in Fig. 4. The value of the mD-Y model (n is variable) indicates lowest in three equations. Error values in CO_2 tend to be small comparing to that in CH_4.

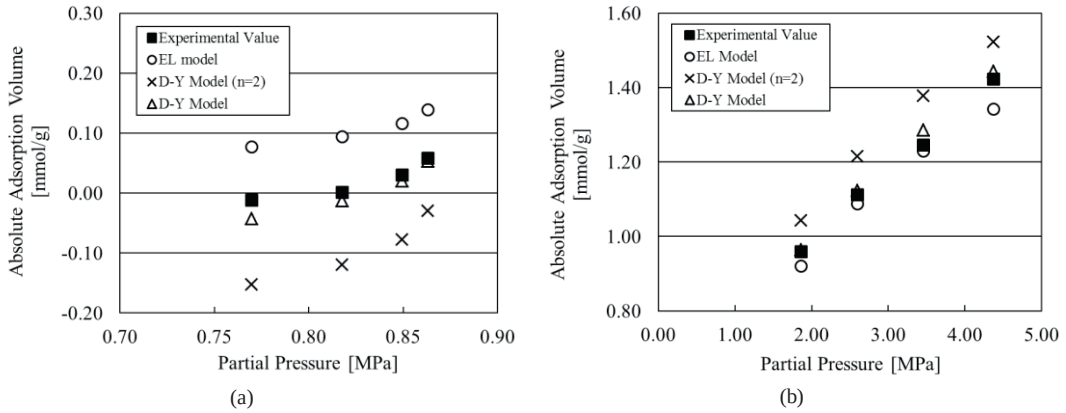

Fig. 3 Absolute adsorption volume of (a) CH_4 and (b) CO_2

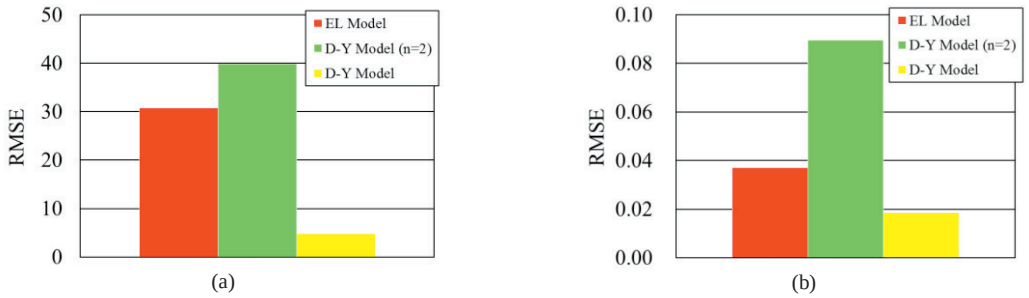

Fig. 4 RMSE of (a) CH_4 and (b) CO_2

Similarly, results of displacement experiments for ternary gases were compared to the theoretical data. The mixture of CO_2 and N_2 (10%:90% and 35%:65%) was injected into the sample cell saturated with

CH_4. Theoretical values were calculated by Eq. (2) and Eq. (9) and results of the absolute adsorption volume and RMSEs are shown in Fig.4 and Fig.5, respectively. RMSEs of the mD-Y model (*n* is variable) was totally smallest in three models. The value of that model was lowest and less than one-fifth of other models in the case of N_2 while RMSE of the mD-Y model (*n* is equal to two) indicated smallest in the case of CH_4 and CO_2.

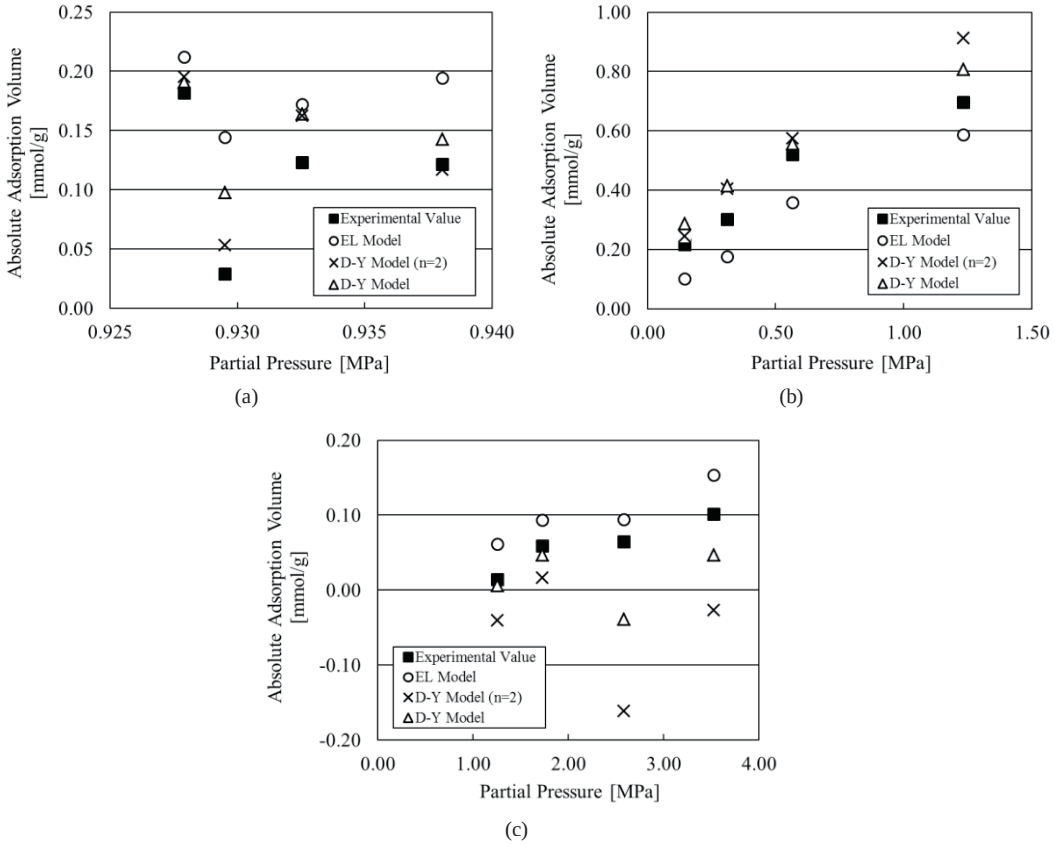

Fig. 5 Absolute adsorption volume of (a) CH_4 (b) CO_2 and (c) N_2

Fig. 6 RMSE of CH_4, CO_2 and N_2

4. Discussion

4.1 Binary gases

Values of RMSEs in adsorbed methane were larger than those in CO_2. One of the reasons is adsorption amount of CH_4 was small and the systematic error greatly affect it. However, RMSEs which were not normalized were almost same between CH_4 and CO_2 while the adsorption volume of CO_2 is about ten times more than that of CH_4. Other reasons, for instance difference of the adsorption mechanism and the adsorption phase density could have been involved.

4.2 Ternary gases

Although RMSEs in N_2 whose adsorption volume was smallest tended to be larger depending on systematic error, the RMSE of the mD-Y model in N_2 was almost the same with that in CH_4 and CO_2. RMSEs of the mD-Y were totally lowest in three models.

While the assumption that the adsorption volume of one adsorbate is decreased by total adsorption volume of all other adsorbate gases was used in this research, there are other studies about extension of the D-A model. One example is using the average maximum adsorption volume instead of the maximum adsorption volume but the definition of it is arguable and results of the calculation using simple arithmetic average did not agree with the experimental data.

In this study, gas density at the standard boiling point and the triple point were assumed as the adsorption phase density. As several compensation formulas depending on the temperature are proposed, this topic is still arguable.

As the number of gas components increased, the RMSE in the EL model became larger than that in mD-Y models. Values of RMSEs in the mD-Y models were relatively low and in almost same order while the largest value of EL model was more than double for the smallest value. These facts imply that mD-Y model is more applicable to multi-component gases adsorption than the EL model. However, additional experiments are required to enhance utility for the model as the numbers of data sets are limited.

5. Conclusion

The modification of D-Y model which was sometimes done in D-A model to enable it to be applicable in the supercritical state was made. Modified D-Y model was compared to the experimental data which was obtained by adsorption and desorption experiments for binary (CH_4 and CO_2) and ternary gases (CH_4, CO_2 and N_2). RMSEs between the experimental data and the theoretical value of two models (the EL model and the mD-Y model) for all gas components were calculated. There was good agreement between the experimental values and the values from the mD-Y model. Although RMSEs of EL model for N_2 tended to become larger than other gases because its adsorption amount is relatively low, RMSEs of the

mD-Y model for nitrogen was less than one fifth of that of the EL model. As a result, RMSEs of the mD-Y model varied less throughout all gases. The mD-Y model is promising model to predict adsorbed and desorbed gas volume in ECBMR. However, treatment of adsorption phase density and additional experiments are still required to enhance utility for the model.

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